Argonne National Laboratory

DENSITY MEASUREMENTS IN GLOVEBOXES

With Density Data on Monobromobenzene, Cast Thorium, Thorium-Uranium, and Thorium-Plutonium Alloys

by

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Metallurgy Division

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INTRODUCTION

The conditions under which measurements in gloveboxes are made differ from those which are made in an ordinary laboratory on an open bench top. Confining space, consideration of access, safety and criticality, the effect of glovebox atmosphere and, in some cases, self-heating of the material under study are factors which influence the measurements. The mechanical features of a chosen method, the degree of control over its variables, the possibility of recalibration after an initial calibration determine the precision of measurements and the attainable accuracy. Unfortunately, all of these factors slow down, to a varying degree, the process of measurement. Thus, the desire to obtain rapid results with alpha-active metals may lead to a conscious neglect of some variables. Yet, in the end, such an approach produces data which are inferior to those that are obtained or obtainable for comparable purposes in a comparable research situation with nonradioactive and less toxic materials.

The work herein reported is aimed at developing a more precise and accurate method of determining density of plutonium-containing materials while working in gloveboxes. Specifically, the measurements are part of an investigation of the constitution and properties of the thorium-uranium-plutonium alloys. Since the techniques of working with plutonium and its alloys are still known to only a small number of people, any intelligent expansion in the utilization of plutonium will greatly depend on the availability of better measurement techniques and of more accurate data than we presently have. Simultaneously, the report is presented in sufficient detail to serve as a guide to those in our laboratory who are charged with making the measurements.

There exists a very extensive literature on density measurements. Good summaries of the available methods and evaluations of the various factors involved are found in A. Weissberger, Physical Methods of Organic Chemistry, in the chapter by N. Bauer[1] on "Determination of Density," and in F. Kohlrausch, Praktische Physik, in the chapter by J. Otto[2] on "Dichte." The important papers on density measurements published by members of the National Bureau of Standards are reprinted in its

Handbook 77[3] on Precision Measurements and Calibration. The paper by C. T. Collet,[4] Simplification of Calculations in Routine Density and Volumetric Determinations, may be specifically mentioned.

STATUS

For the present investigation we have used as standards a stainless steel cylinder weighing about 60 g and a platinum cylinder weighing about 30 g. Their densities as reported by NBS are 7.9025 ± 0.0001 g/cm^3 at 22.72°C and 21.429 ± 0.001 g/cm^3 at 22.87°C, respectively. A local commercial laboratory reported the density of a lot of monobromobenzene (C_6H_5Br) at 20.0°C to be 1.4957_4 g/cm^3, which implies an accuracy of better than 0.0001 g/cm^3. On the other hand, routine density determinations of plutonium and its alloys by the Los Alamos Scientific Laboratory, according to a private communication from F. Schonfeld, are made with a precision of ± 0.03 g/cm^3 and an estimated accuracy of ± 0.05 g/cm^3. These determinations are made by the hydrostatic weighing method with monobromobenzene as a liquid. Similar results are obtained at ANL in routine density measurements in the fabrication of plutonium-bearing fuel elements.[5] An improvement in accuracy and precision by a factor of 10 would certainly be desirable and greatly add to the physical significance of the data.

VARIABLES IN DENSITY MEASUREMENTS
AND METHOD OF CALCULATION

The basic equation

$$\rho = M/V \quad , \tag{1}$$

where ρ is the density, and M and V are the mass and volume of the specimen, is valid for the temperature t if no change takes place while the measurement is being made. If the very convenient hydrostatic weighing method is used for glovebox work, it is thus necessary to ascertain that the specimen, when weighed in air or in some other glovebox atmosphere, is at the same temperature as when it is subsequently weighed in the liquid. Differences between room temperature and that of the liquid are usually negligible in an air-conditioned laboratory when a large tank of water is given sufficient time to attain room temperature. This condition does not exist in a glovebox as will be shown below. In an ordinary laboratory the quantity of liquid (usually water) is large enough and the humidity in the room is sufficiently high and constant that surface phenomena such as evaporation do not affect the temperature of the liquid. The high degree of unsaturation of the atmosphere (in our case nitrogen) desired in a plutonium glovebox enhances greatly the evaporation rate of liquids of low boiling point and causes the temperature of the liquid to be lowered.

This is particularly apparent when, in the course of a day's work, the glove-box temperature rises with room temperature. Apparatus for controlling all of these variables would be rather cumbersome, and it is easier to apply suitable corrections. The applicable equations which are given in the following paragraphs, take into account the buoyancy correction for the nitrogen atmosphere in the glovebox and the above-mentioned temperature variations.

If

ρ_t is the density of specimen at temperature t,

ρ_b the density of the liquid (monobromobenzene), at temperature t,

ρ_{N_2} the density of the nitrogen gas atmosphere at temperature t and barometric pressure p,

M_f the apparent weight of the specimen in the nitrogen atmosphere at temperature t,

M_h the apparent weight of the volume of liquid displaced by the specimen of apparent weight M_f at temperature t,

i.e., if all variables refer to the same temperature t, then

$$\rho_t = \frac{M_f}{M_h} (\rho_b - \rho_{N_2}) + \rho_{N_2} \quad . \tag{2}$$

Since the hydrostatic weighing method requires the specimen to be weighed both in the nitrogen glovebox atmosphere and suspended in the liquid, it is convenient to leave the suspension wire and basket in the liquid throughout the measurements. Thus,

$$M_f = W_{N_2} - T_1 \quad , \tag{3}$$

where

W_{N_2} is the actual as-measured weight of the specimen on the balance pan at temperature t_{N_2}, and

T_1 the actual as-measured weight of the suspension wire as it partially dips into the liquid (the tare).

If, because of some unstable condition, the tare T_1 does not stay constant, it may be necessary to determine the tare before and after determining W_{N_2} and to find T_1 by interpolation.

To determine M_h the specimen is weighed in the liquid, ordinarily at temperature t. We weigh, however, at the temperature t_b and obtain

W_b = the actual as-measured total weight of the specimen plus the tare in the liquid at temperature t_b,

T_2 = the tare at temperature t_b, and

W_{imm} = the actual weight of the specimen immersed in the liquid at temperature t_b, since

$$W_{imm} = W_b - T_2 \quad . \tag{4}$$

Furthermore,

$$M_k = M_f - W_{imm} \quad , \tag{5}$$

where M_k is the apparent weight of the volume of liquid at temperature t_b displaced by the specimen also at the temperature t_b. Then, as shown in Appendix A, equation (2) becomes

$$\rho(t_{N_2}) = \frac{M_f}{M_k} \left\{ \rho_{b(t_b)} [1 + \alpha(t_b - t_{N_2})] - \rho_{N_2} \right\} + \rho_{N_2} \quad , \tag{6}$$

where $\rho_{b(t_b)}$ is the density of the liquid at temperature t_b. The volume coefficient of expansion of the specimen, α, is usually unknown for new alloys and must be estimated. If $(t_b - t_{N_2})$ does not exceed about two degrees the possible error due to this difference in temperature is small. Since, usually, $t_{N_2} > t_b$, it is convenient to write

$$1 + \alpha(t_b - t_{N_2}) = 1 - \alpha(t_{N_2} - t_b) = 1 - \alpha\Delta t \quad ,$$

and equation (6) becomes

$$\rho(t_{N_2}) = \frac{M_f}{M_k} [\rho_{b(t_b)} (1 - \alpha\Delta t) - \rho_{N_2}] + \rho_{N_2} \quad . \tag{6a}$$

Also, since ρ_b changes nearly linearly with temperature over a small temperature range, $\rho_{b(t_b)}$ may be referred to the density at 25°C by

$$\rho_{b(t_b)} = \rho_{25} + \Delta\rho_b(t_{25} - t_b)$$

$$= \rho_{25} + \Delta\rho_b \Delta t'' \quad ,$$

where $\Delta\rho_b$ for monobromobenzene is 0.001374 g/cm^3 for temperatures in the neighborhood of 25°C with sufficient accuracy, and where $\Delta t'' = t_{25} - t_b$.

Thus equation (6) is used in the form

$$\rho(t_{N_2}) = \frac{M_f}{M_k} [(\rho_{b(25)} + \Delta\rho_b \Delta t'')(1 - \alpha\Delta t) - \rho_{N_2}] + \rho_{N_2} \quad . \tag{7}$$

The density ρ_b of the liquid in equations (6) or (7) is derived from the density of the stainless steel standard mentioned above. For this purpose equation (6) becomes

$$\rho_{b(t_b)} = \frac{1}{1 + \alpha(t_b - t_{N_2})} \left[\frac{M_k}{M_f} \left(\rho_{st(t_{N_2})} - \rho_{N_2} \right) \right] + \rho_{N_2} \tag{8}$$

or

$$\rho_{b(t_b)} = \frac{1}{1 - \alpha \Delta t} \left[\frac{M_k}{M_f} \left(\rho_{st(t_{N_2})} - \rho_{N_2} \right) \right] + \rho_{N_2} \quad , \tag{9}$$

where $\rho_{st(t_{N_2})}$ is the density of the stainless steel standard at temperature t_{N_2}. The value of $\rho_{st(t_{N_2})}$ is calculated from the density $\rho_{st(t_r)}$ of the stainless steel standard at the reported temperature t_r from

$$\rho_{st(t)} = \rho_{st(t_r)} \left[1 + \alpha_{st}(t_r - t) \right] \quad , \tag{10}$$

where $\alpha_{st} = 52 \times 10^{-6}\ °C^{-1}$ is the volume coefficient of expansion of type 304 stainless steel and $t_{(N_2)}$ is equal to the t of this equation. For $\rho_{st(t)}$ in the temperature range of 20 to 28°C, see Table III.

Table I

DENSITY (ρ_{N_2}) OF DRY NITROGEN BETWEEN 20 AND 28ºC AT A
BAROMETRIC PRESSURE OF 760 mm Hg

Density at 0ºC: 0.00125051 g/cm³

$$\rho_{N_2(t)} = \frac{0.00125051}{1 + 0.003661\ t} \text{ in g/cm}^3$$

t	N₂	t	N₂	t	N₂	t	N₂
20.0	0.001165	22.0	0.001157	24.0	0.001150	26.0	0.001142
20.1	0.001165	22.1	0.001157	24.1	0.001149	26.1	0.001141
20.2	0.001164	22.2	0.001157	24.2	0.001149	26.2	0.001141
20.3	0.001164	22.3	0.001156	24.3	0.001148	26.3	0.001141
20.4	0.001164	22.4	0.001156	24.4	0.001148	26.4	0.001140
20.5	0.001163	22.5	0.001155	24.5	0.001148	26.5	0.001140
20.6	0.001163	22.6	0.001155	24.6	0.001147	26.6	0.001140
20.7	0.001162	22.7	0.001155	24.7	0.001147	26.7	0.001139
20.8	0.001162	22.8	0.001154	24.8	0.001146	26.8	0.001139
20.9	0.001162	22.9	0.001154	24.9	0.001146	26.9	0.001138
21.0	0.001161	23.0	0.001153	25.0	0.001146	27.0	0.001138
21.1	0.001161	23.1	0.001153	25.1	0.001145	27.1	0.001138
21.2	0.001160	23.2	0.001153	25.2	0.001145	27.2	0.001137
21.3	0.001160	23.3	0.001152	25.3	0.001145	27.3	0.001137
21.4	0.001160	23.4	0.001152	25.4	0.001144	27.4	0.001137
21.5	0.001159	23.5	0.001151	25.5	0.001144	27.5	0.001136
21.6	0.001159	23.6	0.001151	25.6	0.001144	27.6	0.001136
21.7	0.001158	23.7	0.001151	25.7	0.001143	27.7	0.001135
21.8	0.001158	23.8	0.001150	25.8	0.001143	27.8	0.001135
21.9	0.001158	23.9	0.001150	25.9	0.001142	27.9	0.001135
22.0	0.001157	24.0	0.001150	26.0	0.001142	28.0	0.001134

To obtain density at other barometric pressures
multiply by appropriate ratio of Table II.

For the calculation of the density ρ_{N_2} in equations (7) and (9) at temperature t (in °C) and barometric pressure p for the very dry nitrogen gas in our gloveboxes, the gas laws are applicable:

$$\rho_{N_2} = \frac{0.00125051}{1 + 0.003661\ t} \; \frac{p}{760} \quad ,$$

where 0.00125051 g/cm³ is the density of nitrogen gas at 0°C and at 760 mm Hg. The value of ρ_{N_2} for a given temperature and pressure may be obtained from Tables I and II by multiplying the appropriate values.

Finally, the density data obtained from equation (7) may be reduced to 25°C values by means of the equation

$$\rho_{(25)} = \rho_t \left[1 + \alpha(t - 25.00) \right] \quad ,$$

where $(t - 25.00)$ may be either positive or negative.

Table II

RATIO (R) OF BAROMETRIC PRESSURE p OVER
STANDARD PRESSURE OF 760 mm Hg FOR
PRESSURES OF 720 TO 760 mm Hg

p	R	p	R
720	0.9474	740	0.9737
721	0.9487	741	0.9750
722	0.9500	742	0.9763
723	0.9513	743	0.9776
724	0.9526	744	0.9789
725	0.9539	745	0.9803
726	0.9553	746	0.9816
727	0.9566	747	0.9829
728	0.9579	748	0.9842
729	0.9592	749	0.9855
730	0.9605	750	0.9868
731	0.9618	751	0.9881
732	0.9632	752	0.9895
733	0.9645	753	0.9908
734	0.9658	754	0.9921
735	0.9671	755	0.9934
736	0.9684	756	0.9947
737	0.9697	757	0.9960
738	0.9711	758	0.9974
739	0.9724	759	0.9987
740	0.9737	760	1.0000

P. P.

13	
1	1.3
2	2.6
3	3.9
4	5.2
5	6.5
6	7.8
7	9.1
8	10.4
9	11.7

14	
1	1.4
2	2.8
3	4.2
4	5.6
5	7.0
6	8.4
7	9.8
8	11.2
9	12.6

Table III

DENSITY OF STANDARD STAINLESS STEEL SPECIMEN BETWEEN 20 AND 28°C

Density (ρ) by NBS: 7.9025 g/cm^3 at t = 22.72°C
Volume Coefficient of Expansion α = 51.8 x 10^{-6} °C^{-1}

$$\rho_{st(t)} = \rho_{22.72} [1 + \alpha(22.72 - t)] \text{ g/cm}^3$$

Temp (°C)	Density (g/cm^3)	Temp (°C)	Density (g/cm^3)	Temp (°C)	Density (g/cm^3)	Temp (°C)	Density (g/cm^3)
20.0	7.9036	22.0	7.9028	24.0	7.9020	26.0	7.9012
20.1	7.9036	22.1	7.9028	24.1	7.9020	26.1	7.9011
20.2	7.9035	22.2	7.9027	24.2	7.9019	26.2	7.9011
20.3	7.9035	22.3	7.9027	24.3	7.9019	26.3	7.9010
20.4	7.9034	22.4	7.9026	24.4	7.9018	26.4	7.9010
20.5	7.9034	22.5	7.9026	24.5	7.9018	26.5	7.9010
20.6	7.9034	22.6	7.9025	24.6	7.9017	26.6	7.9009
20.7	7.9033	22.7	7.9025	24.7	7.9017	26.7	7.9009
20.8	7.9033	22.8	7.9025	24.8	7.9016	26.8	7.9008
20.9	7.9032	22.9	7.9024	24.9	7.9016	26.9	7.9008
21.0	7.9032	23.0	7.9024	25.0	7.9016	27.0	7.9007
21.1	7.9032	23.1	7.9023	25.1	7.9015	27.1	7.9007
21.2	7.9031	23.2	7.9023	25.2	7.9015	27.2	7.9007
21.3	7.9031	23.3	7.9023	25.3	7.9014	27.3	7.9006
21.4	7.9030	23.4	7.9022	25.4	7.9014	27.4	7.9006
21.5	7.9030	23.5	7.9022	25.5	7.9014	27.5	7.9005
21.6	7.9030	23.6	7.9021	25.6	7.9013	27.6	7.9005
21.7	7.9029	23.7	7.9021	25.7	7.9013	27.7	7.9005
21.8	7.9029	23.8	7.9021	25.8	7.9012	27.8	7.9004
21.9	7.9028	23.9	7.9020	25.9	7.9012	27.9	7.9004
22.0	7.9028	24.0	7.9020	26.0	7.9012	28.0	7.9003

EXPERIMENTAL APPARATUS

The measurement of density involves the determination of weight, temperature, barometric pressure, and the selection of a suitable liquid.

Weighing

Because of the limitation of size and weight and the high density of many plutonium-bearing specimens, a semi-microbalance was selected. The balance was a single-pan substitution balance (see Figures 1 and 2), thought to be attractive because of its greater ease of manipulation and readability in glovebox work. It was expected and turned out to be rather more sensitive to temperature fluctuations than a standard analytical balance with equal arms. Nevertheless, the balance was retained because of its handling characteristics. Initially, the balance was placed on a bridge to accommodate the liquid underneath. Unfortunately, vibrations caused by the building ventilation made it impossible to use the balance in this way and only through placing the balance firmly on the bottom of the glovebox and the glovebox on a 900-lb concrete base was it possible to make consistent weighings. The suspension of the balance pan was shortened to accommodate a dish of 13 cm (5 in.) in diameter, 7.6 cm (3 in.) in height and of 800-ml capacity inside the balance case.
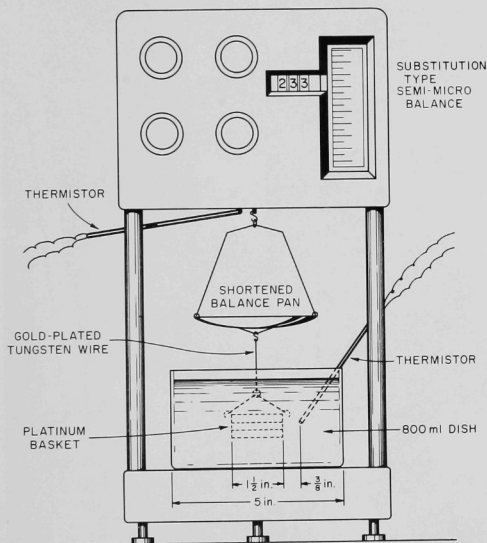
Figure 1. Scheme of Density Balance

A gold-plated tungsten suspension wire holding a platinum wire basket was attached to the pan. It was thus possible to weigh the specimen either in the glovebox atmosphere or immersed in the liquid without changing the setup simply by placing it either onto the pan or into the basket. The level of the liquid remained constant throughout the weighings of a particular specimen. Small radium-containing disks placed near the knife edges took care of static charges. No difficulties were experienced from the flow of nitrogen gas through the glovebox since its rate of flow of

2.8 liters/min (0.1 ft^3/min) was low, but the movement of the gloves during operation greatly influenced the weighing even when the balance case was closed. It is suspected that this effect of glove movement is largely due to the design of the damping mechanism, an air dash pot, with which single-pan substitution balances are equipped. Since the operator may not move his arms while the balance seeks its equilibrium position, the balance will be replaced by one having a magnetic damping device and recently made available to us by Wm. Ainsworth and Sons, Golden, Colorado. It is expected that this modification will ease our operating problem.
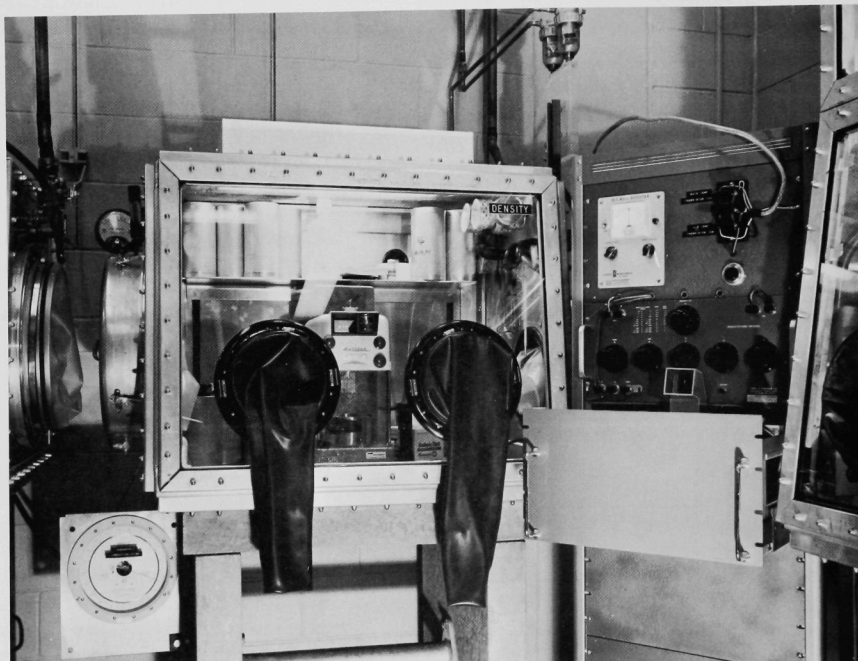
Figure 2. Density Glovebox

In weighing, another important factor requiring control is temperature. Initial temperature measurements showed that the glovebox, of 0.69-m^3 (24.5-ft^3) volume, was heated appreciably by the two fluorescent 30-w lamps on top of the glovebox. Their removal and subsequent reliance on room-temperature lighting greatly improved the weighing conditions. Still, the lamp which is part of the optical system of the balance created enough heat to influence the results. Heat insulation or, better still, the use of a heat source external to the balance case, will alleviate this

problem. Figure 3 shows the temperature changes that took place during a Saturday in the summer at the time we began to make measurements. The glovebox temperature rose steadily during such a period.

Figure 3. Temperature and Tare Variations
during Density Measurements

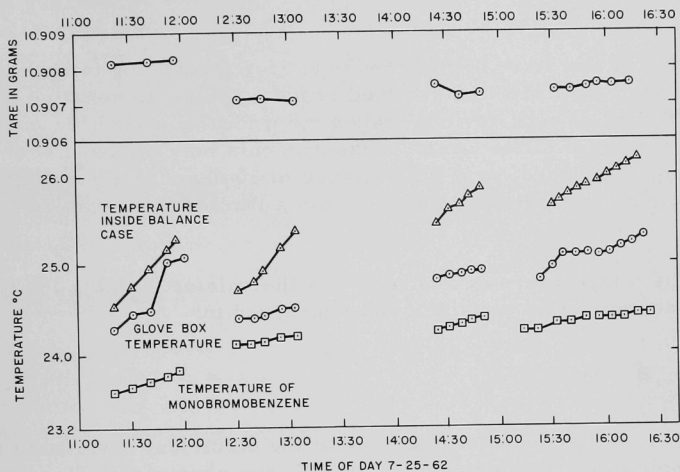Even though the laboratory is air conditioned, a temperature rise in the glovebox cannot be avoided. Periods of work interruption did not significantly affect this temperature rise. The temperature inside the balance case, however, rises steeply during work periods and falls again during periods of work interruption. The temperature of the liquid inside the balance case, because of its large heat capacity, follows the same temperature pattern as the glovebox. Because of these temperature variations, the weight of the basket suspended in the liquid (the tare) also changes with time and may make it necessary to bracket each weighing between two tare determinations.

Temperature Measurements

Ordinarily temperature measurements outside a glovebox are satisfactorily made with precision mercury-in-glass thermometers. Once calibrated they require checking of the ice point as they change slowly with time. This is inconvenient in glovebox work. Also, small size mercury-in-glass thermometers of sufficient accuracy are not commercially available. Their readability through the sloping front glovebox window and the window of the balance case would be poor.

The National Bureau of Standards uses a platinum-resistance thermometer to measure the temperature of the large volume of water located underneath the balance. The large size of the resistance thermometer is not suitable for measuring the temperature of a small volume of liquid inside the balance case.

Thermistors are highly convenient for measuring temperatures near room temperature in a confined space. The large negative temperature coefficient of such devices makes them ideally suited for measuring small temperature differences. Measurements may be made with a Wheatstone bridge and since, say, a resistance of 80 ohms is equivalent to 1°C, good precision is easily obtainable within a limited temperature range of 10°C.

The temperature dependence of a thermistor suitable for temperature measurements is satisfactorily expressed by

$$\log R = \frac{1}{T} C_1 + C_2 \quad , \tag{11}$$

where $\log R$ is the decadic logarithm of the electrical resistance in ohms, T the absolute temperature, and C_1 and C_2 are constants. This equation is equivalent to Kittel's equation[6] for the intrinsic electrical conductivity of a semiconductor:

$$\log \rho = \log A + (E_g/2kT) \quad , \tag{12}$$

where ρ is the intrinsic resistivity in the intrinsic temperature range, i.e., the temperature range in which the electrical properties of a semiconductor are not essentially modified by impurities in the crystal, E_g is the energy gap between the valence and conduction bands, k is the Boltzmann constant, T is the absolute temperature, and A is a constant. The intrinsic temperature range may extend over a couple of hundred degrees Kelvin as shown by J. A. Becker[6] for Fe_2O_3, Cu_2O, Si, and Ge. For thermistors in which impurity conduction plays an important role, equations (11) and (12) should not hold. However, over the very small temperature interval near room temperature in which we are interested, equation (11) is still applicable; in our case the maximum deviation from linearity for a given resistance between 20°C and 40°C was only 0.005°C. Also, equation (11) is valid only at a constant low current and, therefore, calibration and measurements are now made with a constant current of 100 μamp.

The current for the measurements is supplied by a lead storage battery via a variable resistor. The current is measured by the voltage drop across a 100-ohm standard resistance in series with the measuring arm of the Wheatstone bridge. The 100-ohm resistance is then deducted from the measured value.

We have used a glass-probe thermistor with a room-temperature resistance of about 2,000 ohms. For calibration the thermistor is placed in a thermostat, and its resistance during 100-μamp current flow is measured by a guarded Wheatstone bridge. The same temperature is measured with a calibrated platinum-resistance thermometer and a Mueller bridge. Measurements are made at 1°C temperature intervals. The least-squares fit of the data gives both the constants of equation (11) and their standard deviations, and a table of correlated values for intervals of 0.1 ohm are computed with an IBM 704F computer (Program Library 1448/MET141).

The actual temperature measurements in the glovebox of the balance case and the liquid are made with a less precise Wheatstone bridge. The temperature measurements are correct to 0.01°C.

Barometric Pressure

A precision aneroid manometer capable of determining the barometric pressure with an accuracy of 1 part in 1000 and calibrated at ANL's Weather Station was connected to the glovebox. A filter protected the inlet to the manometer from contamination.

The Liquid

The use of water as a liquid is precluded in a dry nitrogen atmosphere. Water readily attacks many plutonium alloys. Carbon tetrachloride was rejected because its high rate of evaporation (boiling point 76.8°C) caused a significant lowering of its temperature, more than compensating for the general temperature increase of the apparatus. Monobromobenzene (C_6H_5Br) (density about 1.5 g/ml, boiling point 155°C), used by Los Alamos and other AEC installations, despite disadvantages, was adopted after some trials for lack of something better. Van Vestrout and Shuck[7] have shown that it softens neoprene. Neoprene exposed to the monobromobenzene (for a period of $2\frac{1}{2}$ hr) loses its strength and is easily pulled apart. The neoprene, however, is returned to its original state after the liquid has evaporated. Monobromobenzene vapor diffuses easily through the gloves, and its characteristic odor is detected in the laboratory whenever it is worked with inside the glovebox.

The following rules should be strictly observed when working with monobromobenzene:

1. Monobromobenzene shall be stored only in brown bottles with tight-fitting caps when not in use. A quantity of liquid may be left in the open dish inside the balance case for a short period of time, e.g., during the lunch period.

2. An unbreakable container shall be used for storage if possible; otherwise a secondary protective container shall be employed.

3. If monobromobenzene is spilled, the spillage shall be wiped up immediately and special attention shall be given to neoprene parts.

4. Waste cans containing small quantities of monobromobenzene shall be removed from the glovebox and properly disposed of at the end of each work day.

5. Gloves which have been exposed to a quantity of liquid monobromobenzene may only be used with care and no great stress shall be applied to material that may have been saturated.

6. Folding the gloves inside the glovebox increases the number of pockets where vapor may collect. Tie the gloves at the outside.

7. Use a fan to increase the air flow near the glovebox and disperse the toxic vapors that have diffused to the outside.

Our data (see Table IV) show that the density of monobromobenzene decreases with time. The density also varies while the liquid is being used, increasing, decreasing or not changing at all during a day's operation. Since the liquid is returned to its supply bottle after use, a complex pattern will result.

Table IV

DENSITY CHANGES OF MONOBROMOBENZENE

Date 1962	Time of Day	Density at 25°C (g/cm^3)	Standard Used
6-1	11:32	1.4859	SS*
6-4	11:00	1.4849	Pt
6-4	16:05	1.4855	SS
6-6	14:52	1.4841	SS
6-6	16:28	1.4846	SS
6-8	11:32	1.4831	SS
6-8	12:05	1.4833	Pt
6-8	13:21	1.4835	SS
6-8	14:32	1.4840	Pt
6-8	16:25	1.4840	SS
6-13	12:00	1.4817	SS
6-13	13:34	1.4820	Pt
6-13	14:10	1.4819	SS
7-25	11:50	1.4839	SS
7-25	13:55	1.4837	SS
7-25	16:10	1.4832	SS
7-26	10:00	1.4836	SS
7-26	16:50	1.4829	SS
7-27	9:35	1.4833	SS
7-27	16:45	1.4819	SS
10-19	10:35	1.4799	SS
10-19	14:33	1.4801	SS
10-19	16:26	1.4800	SS
10-27	9:07	1.4798	SS
10-27	14:28	1.4792	SS
10-27	13:38	1.4796	SS

*SS = Stainless Steel

It is suggested that the general decrease in density is the result of photochemical decomposition. A day's change may be the combined result of photochemical decomposition, the temperature effect of evaporation, a temperature gradient in the liquid, or other, still unknown causes. Since this behavior is not predictable, it is advisable to bracket a series of density determinations by density determinations of the liquid with the stainless steel standard. It is not surprising that the literature data for the density of monobromobenzene are higher than the values reported in Table IV since they refer to a highly refined compound. The temperature coefficient, however, is not affected.

DISCUSSION

The Effect of Self-heating of Plutonium

The general applicability of equation (6) [equation (11) of Appendix A] depends upon the rate with which the specimen reaches its temperature equilibrium with its surroundings. For specimens containing a limited amount of plutonium it may be assumed that this occurs rather quickly and that the specimen and the surrounding liquid then are at the same temperature. Where self-heating is significant, as in the case with pure plutonium, additional temperature corrections may be necessary to compensate for the difference in volume of the specimen and the temperature gradient in the liquid.

To determine such a temperature difference we have placed a plutonium specimen in a beaker filled with monobromobenzene and measured the temperature in the center of the specimen, the temperature close to its surface, and the temperature at distances of 10 mm and 25 mm away from the specimen. The temperatures were measured with a calibrated thermistor. The specimen was a 35.7-g piece about 10 x 13 x 22 mm. A hole of 2-mm diameter was drilled into the center of the specimen parallel to its longest side to accommodate the thermistor. The temperature differences between the specimen and the liquid at distances of 10 mm and 25 mm were uniformly 0.86 to 0.87°C. The temperature differences between the inside of the specimen and the liquid in its immediate vicinity at 1.5-mm and 3-mm distance varied and were 0.55, 0.82, 0.77, and 0.83°C. It is apparent that the volume of the liquid in the vicinity of the specimen that is affected by the self-heating specimen is small and that the temperature gradient extends only over a rather thin boundary layer.

Thus an error is introduced into the calculation when, instead of the true specimen temperature, the mean temperature of the liquid is used for both the liquid and the specimen. This maximum possible error may be calculated as follows.

If $\Delta\rho$ is this error and $\Delta\rho_{b_x}$ the change in density of the monobromo-benzene caused by the observed temperature difference of Δt_x, equation (6a):

$$\rho(t_{N_2}) = \frac{M_f}{M_k} \left[\rho_{b(t_b)}(1-\alpha\Delta t) - \rho_{N_2}\right] + \rho_{N_2} \quad , \tag{6a}$$

becomes

$$\rho(t_{N_2}) + \Delta\rho = \frac{M_f}{M_k}\left[(\rho_{b(t_b)} - \Delta\rho_{bx})(1-\alpha\Delta t + \alpha\Delta t_x) - \rho_{N_2}\right] + \rho_{N_2} \quad . \tag{13}$$

Subtraction of equation (6a) from equation (13) yields

$$\Delta\rho = \frac{M_f}{M_k}\left[\rho_{b(t_b)}\alpha\Delta t_x - \Delta\rho_{bx}(1-\alpha\Delta t + \alpha\Delta t_x)\right] \quad . \tag{14}$$

For

$$\Delta t_x = 0.87°C \text{ as shown above,}$$

$$\alpha = 165 \times 10^{-6} \text{ cm/cm-}°C \text{ for plutonium,}$$

$$\rho_{b(t_b)} = 1.48 \text{ g/cm}^3 \text{ for monobromobenzene,}$$

$$\Delta\rho_{b_x} = 0.87 \times 0.001374 = 0.001195 \text{ g/cm}^3,$$

$$\Delta t = 1°C \text{ (an average value),}$$

we obtain,

$$\Delta\rho_b = \frac{M_f}{M_k}\left[0.000213 - 0.001195\right] \text{ g/cm}^3 \quad . \tag{15}$$

For $M_f/M_k \sim 13.5$, which is the case for a plutonium alloy,

$$\Delta\rho \sim -0.009 \text{ g/cm}^3 \quad .$$

This is a large error caused mainly by the temperature effect on the liquid $\Delta\rho_{b_x}$ in equation (14). It is because of this that the second term in brackets in equation (15) is much larger than the first. The error is too large to be neglected when making measurements with pure plutonium. The error may be reduced by selecting a smaller specimen and choosing a more favorable surface-to-volume ratio for better heat dissipation. When working with dilute plutonium alloys the error becomes small enough to fall within the experimental error of the method.

The Effect of the Vapor Pressure of Monobromobenzene

Another question raised in the discussion on the effect of various variables on the density measurements concerned the effect of the vapor pressure of the monobromobenzene. This effect is negligible and well below the experimental error, as shown in Appendix B.

DATA

The densities of two series of arc-melted thorium alloys were measured. The first series, whose densities are given in Table V, was prepared from a commercial grade of thorium and dingot uranium. The second series, with densities as shown in Table VI, was prepared from crystal bar thorium and high-purity plutonium. The standard deviations of the two sets of data are 0.004 g/cm^3 and 0.005 g/cm^3, respectively. Although these are an order of magnitude better than those referred to above, the accuracy of the data obtained by the National Bureau of Standards for measurements outside the glovebox is not attained. Yet, the greatly improved results are sufficiently good to give meaningful structural information.

Table V

DENSITY AND SPECIFIC VOLUME OF COMMERCIAL THORIUM
AND ARC-MELTED THORIUM-URANIUM ALLOYS

Number	Alloy Nominal w/o		Density at 25°C (g/cm^3)	Mean Value at 25°C (g/cm^3)	Spec Volume at 25°C (cm^3/g)
	Th	U			
B751	100	0	11.679 11.676	11.678	0.08563
B752	90	10	12.113 12.112	12.113	0.08256
B753	80	20	12.604 12.608	12.606	0.07933
B754	70	30	13.155 13.163	13.159	0.07599
B755	60	40	13.762 13.764	13.763	0.07266
B756	50	50	14.439 14.437	14.438	0.06927
B760	0	100	19.009 19.116	19.013	0.05260

Table VI

DENSITY AND SPECIFIC VOLUME OF CRYSTAL BAR THORIUM
AND THORIUM-PLUTONIUM ALLOYS

Number	Alloy Nominal w/o		Density at 25°C (g/cm³)	Mean Value at 25°C (g/cm³)	Spec Volume at 25°C (cm³/g)
	Th	Pu			
B772	100	0	11.713 11.717	11.715	0.08536
B766	90	10	11.913 11.916	11.914	0.08393
B767	80	20	12.134 12.127	12.131	0.08244
B768	70	30	12.367 12.374	12.371	0.08084
B769	60	40	12.741 12.746	12.744	0.07847
B770	50	50	13.139 13.139	13.139	0.07611
B773	40	60	13.660 13.670	13.665	0.07318

A plot of the specific volume versus composition of a series of
thorium-plutonium alloys gives the linear relationship expected from two-
phase alloys (see Figure 4) as well as a linear relationship for the solid
solutions of plutonium and thorium. The intersection of the curves in-
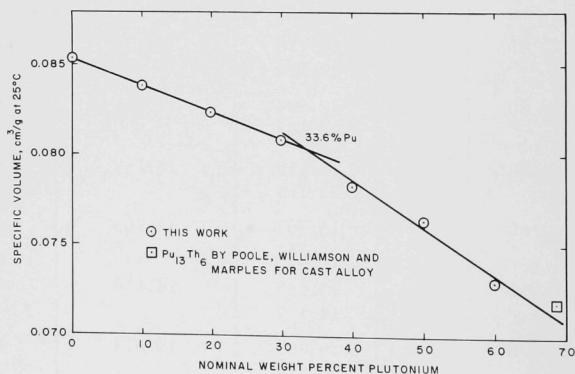dicates the limit of solid solubility. Binary thorium-uranium alloys show

Figure 4. Specific Volume of Arc-melted High-
purity Thorium-Plutonium Alloys

the same phenomenon (see Figure 5). Density variations with structure do show up particularly well in these two systems in which the density differences between the boundary phases are large. In the thorium-uranium system these phases are α thorium-uranium solid solution and α uranium. In the thorium-plutonium system they are α thorium-plutonium solid solution and the compound $Pu_{13}Th_6$ (density 13.96 g/cm^3).[8]
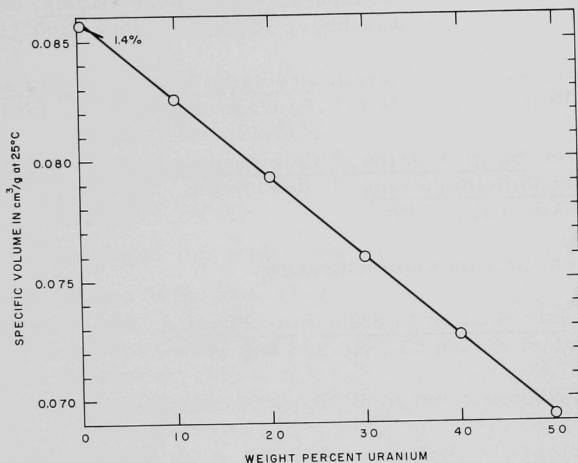

Figure 5. Specific Volume of Arc-melted High-
purity Thorium-Uranium Alloys

SUMMARY

By taking into consideration temperature differences between the glovebox atmosphere and the liquid, it was possible to make density measurements in gloveboxes by the hydrostatic weighing method with monobromobenzene as a liquid with an accuracy of ±0.005 g/cm^3. This is an improvement by an order of magnitude over the prior state. This accuracy allows one to detect structural changes in thorium-uranium and thorium-plutonium alloys.

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ACKNOWLEDGMENT

APPENDIX A

The Density Equation Corrected for Temperature Variations

C. T. Collet[4] has shown that the mass of a specimen when it is weighed on a substitution-type balance in air, is given by

$$M_s = M_f \left(1 - \frac{\rho_a}{\rho_f}\right) + V_s \, \rho_a \quad , \tag{1}$$

where

M_s is the mass of the specimen,

M_f the weight removed to restore equilibrium,

ρ_a the density of the air,

ρ_f the density of the weight, and

V_s the volume of the specimen.

This equation is valid when the specimen and the weights have the same temperature as the surrounding atmosphere. The equation remains unchanged when a basket is suspended from the pan into a liquid and its weight and buoyancy are compensated for by a tare weight, provided that the level of the liquid remains the same and forces of surface tension on the suspension wire are negligible.

Collet also has shown that upon weighing the specimen first in air, then in the liquid,

$$B_s' - B_s = M_h - B_h \quad , \tag{2}$$

where

B_s' is the buoyancy of the specimen in the liquid,

B_s the buoyancy of the specimen in air, and

M_h and B_h the weight and its buoyancy necessary to restore equilibrium when the specimen is immersed in the liquid.

If the specimen, the liquid, and the weights are at the same temperature, that of the surrounding atmosphere, equation (2) is equal to

$$V_s \, (\rho_\ell - \rho_a) = M_h - \frac{M_h}{\rho_h} \, \rho_a \quad , \tag{3}$$

where

ρ_ℓ is the density of the liquid and

ρ_h the density of the weight.

Equation (3) may be rewritten as

$$V_s = M_h \frac{\frac{(1-\rho_a)}{\rho_h}}{\rho_\ell - \rho_a} \, . \tag{4}$$

By dividing equation (4) into equation (1) and making $\rho_f = \rho_h$, we obtain for the density ρ_s of the specimen at the constant temperature t the well-known equation

$$\rho_s = \frac{M_s}{V_s} = \frac{M_f}{M_h} (\rho_\ell - \rho_a) + \rho_a \, . \tag{5}$$

If, however, the temperature of the liquid, t', is different from that of the surrounding atmosphere, t, and if it is assumed that the specimen rather quickly attains the temperature of the liquid after it has been transferred from the pan onto the basket, then equation (2) changes to

$$B_s'' - B_s = M_k - B_k \, , \tag{6}$$

where

B_s'' is the buoyancy of the specimen in the liquid at temperature t',

B_s remains the buoyancy of the specimen in air at temperature t, and

M_k and B_k are the weight at temperature t and the buoyancy required to restore equilibrium.

The equivalent of equation (3) then becomes

$$V_s' \rho_\ell' - V_s \rho_a = M_k - \frac{M_k}{\rho_k} \rho_a \, , \tag{7}$$

where

V_s' is the volume of the specimen at temperature t',

ρ_ℓ' the density of the liquid at temperature t', and

ρ_k the density of the weight,

or

$$V_s' \rho_\ell' - V_s \rho_a = M_k \left(1 - \frac{\rho_a}{\rho_k}\right) \, . \tag{8}$$

Since

$$V_s' = V_s [1 + \alpha(t' - t)] \quad , \tag{9}$$

where

α is the volume coefficient of expansion of the specimen, equation (8) becomes

$$V_s \, \rho_\ell' \, [1 + \alpha(t' - t)] - V_s \, \rho_a = M_k \left(1 - \frac{\rho_a}{\rho_k}\right)$$

or

$$V_s = M_k \frac{1 - \dfrac{\rho_a}{\rho_k}}{\rho_\ell' \, [1 + \alpha(t' - t)] - \rho_a} \quad . \tag{10}$$

Upon calculating ρ_s from equations (1) and (10), and equating $\rho_f = \rho_k$, we obtain

$$\rho_s = \frac{M_s}{V_s} = \frac{M_f}{M_k} \{\rho_\ell' \, [1 + \alpha(t' - t)] - \rho_a\} + \rho_a \quad . \tag{11}$$

In comparing equation (11) with equation (5), we see that only the volume change of the specimen and the density of the liquid enter the density formula when the temperature of the liquid differs from that of the surrounding atmosphere.

This relation may be used to determine the density of a liquid by means of a standard specimen. Equation (11) then converts to

$$\rho_\ell' = \frac{1}{1 + \alpha(t' - t)} \left[\frac{M_k}{M_f}(\rho_{st} - \rho_a) + \rho_a\right] \quad . \tag{12}$$

It should be noted that ρ_ℓ' is the density of the liquid at temperature t', whereas ρ_{st} is the density of the standard at temperature t.

In the present case, in which monobromobenzene is used as a liquid of density ρ_b at temperature t_b in a glovebox with a nitrogen atmosphere of density ρ_{N_2} at a temperature t_{N_2} and pressure p, and a stainless steel specimen of density ρ_{st} is used as a standard, the general equations (11) and (12) revert to

$$\rho(t_{N_2}) = \frac{M_f}{M_k} [\rho_{b(t_b)} (1 - \alpha \triangle t) - \rho_{N_2}] + \rho_{N_2} \tag{13}$$

and

$$\rho_{b(t_b)} = \frac{1}{1 - \alpha \Delta t} \left[\frac{M_k}{M_f} (\rho_{st(t_{N_2})} - \rho_{N_2}) + \rho_{N_2} \right] \quad , \tag{14}$$

where

$$\Delta t = t_{N_2} - t_b \quad .$$

APPENDIX B

The Effect of the Vapor Pressure of Monobromobenzene
on the Density Measurements

In the discussions regarding the effect of various variables on the density measurements, the question of the effect of the vapor pressure of the monobromobenzene was raised. The following considerations are intended to establish the maximum error that may occur when the nitrogen atmosphere of the glovebox is saturated with vapor in contact with the liquid. This entails:

a. the determination of the partial vapor pressure of the bromobenzene;

b. the calculation of its effect on the density of the nitrogen atmosphere;

c. the evaluation of the effect of the density changes of the nitrogen atmosphere on the density of the bromobenzene and ultimately on that of the specimen.

The Partial Vapor Pressure of Monobromobenzene

The pressure p of the pure saturated vapor in contact with the liquid was obtained by extrapolation to 25°C from vapor pressure measurements by Ramsay and Young[9] between 120 to 157°C by means of the relationship

$$\log p = (A/T) + B \quad ,$$

where A and B are constants, and T is the absolute temperature. The equation

$$\log p = (-2061.4/T) + 7.6844$$

yields a vapor pressure of 5.85 mm Hg at 25°C.

To determine the actual conditions in the glovebox, a small dish of 60-mm diameter containing 32.7 g of bromobenzene was exposed to the glovebox atmosphere and weighed at half-hour intervals. No nitrogen was flowing through the glovebox during this experiment, but the glovebox atmosphere was maintained at its normal negative pressure of 12.7 mm (0.5 in.) of water. The weight losses were 0.152, 0.157, 0.143, and 0.150 g during each half-hour period, equivalent to about 2.4 g for an 8-hr work day. During the subsequent night period of 16 hr, the normal nitrogen flow of 5.7ℓ/min (0.2 ft^3/min) was restored. The total weight loss was 4.23 g for this period, equivalent to 2.1 g for an 8-hr day. Since the glovebox temperature was lower during the night, a smaller weight loss may be expected. The slow nitrogen throughput does not significantly change the rate of evaporation.

If one assumes that all the vapor evolved during an 8-hr period remains in the box of 694-liter (24.5-ft^3) volume, the resultant partial vapor pressure would be about 4.1 mm Hg at the average temperature of 26.2°C. At this temperature the saturated vapor pressure is 6.2 mm Hg. These experiments and calculations are good enough to show that a relative humidity of 60 to 70% bromobenzene may be expected under current glovebox conditions.

In the following calculations the saturated vapor pressure at 25°C of 5.85 mm Hg was used as being representative of actual glovebox conditions.

The Density of the Humid Gas

From the gas laws and the definition of density as $\rho = M_0/V_0$, where M_0 is a gram-mole of an ideal gas and V_0 its volume, it can be derived that the density of a gas at the absolute temperature T and the barometric pressure B, containing a vapor of partial pressure e, is

$$\rho = \rho_0 \frac{273.13}{T} \frac{e\left(1 - \frac{M_b}{M_g}\right)}{760} , \tag{1}$$

where ρ_0 is the density of the dry gas at 273.13°C and 760 mm Hg, and M_b and M_g the molecular weights of the vapor and the gas, respectively. Since most of our measurements are made near 25°C and 740 mm Hg, equation (1) may be written as

$$\rho_{(25°C, 740, e)} = \rho_{N_2(25°C, 740)} \frac{740 - e\left[1 - (M_b/M_{N_2})\right]}{740} , \tag{2}$$

where the subscripts indicate the specific condition, and M_b and M_{N_2} are the molecular weights of the bromobenzene and nitrogen, respectively. For

$$\rho_{N_2(25°C, 740)} = 0.001116 \text{ g/cm}^3 \text{ (see Tables I and II)} ,$$

$$M_b/M_{N_2} = 5.6047 ,$$

$$e = 5.85 \text{ mm Hg at 25°C} ,$$

we obtain

$$\rho_{N_2(25°C, 740, e)} = 0.001157 \text{ g/cm}^3 ,$$

so that

$$\rho_{N_2(25°C, 740, e)} - \rho_{N_2(25, 740)} = \Delta\rho_{N_2} = 0.000041 \text{ g/cm}^3 .$$

This is the maximum density change that the nitrogen gas atmosphere may undergo at 25°C and 740 mm Hg pressure.

The Effect of the Density Change of the Glovebox Atmosphere on the Specimen Density

From equation (5) of Appendix A it follows that at constant temperature

$$\rho_b = (M_h/M_f)(\rho_{st} - \rho_{N_2}) + \rho_{N_2} \quad , \tag{3}$$

where ρ_b is the density of the bromobenzene and ρ_{st} that of the standard. If the density ρ_{N_2} changes by $\Delta\rho_{N_2}$, equation (3) becomes

$$\rho_b' = (M_h/M_f)[\rho_{st} - (\rho_{N_2} + \Delta\rho_{N_2})] + \rho_{N_2} + \Delta\rho_{N_2} \quad . \tag{4}$$

Subtracting equation (3) from equation (4), we obtain

$$\rho_b' - \rho_b = \Delta\rho_b = \Delta\rho_{N_2}[1 - (M_h/M_f)] \quad . \tag{5}$$

In our measurements, M_h/M_f is approximately 0.19 for stainless steel. Thus, with $\Delta\rho_{N_2} = 0.000041$ g/cm^3 maximum, we obtain

$$\Delta\rho_b = 0.000033 \text{ g/cm}^3 \text{ max} \quad ,$$

which is less than the experimental error of the density measurements. For the density of the specimen itself the same approach gives

$$\rho_s = (M_f/M_h)(\rho_b - \rho_{N_2}) + \rho_{N_2} \quad ;$$

$$\rho_s' = (M_f/M_h)(\rho_b + \Delta\rho_b - \rho_{N_2} - \Delta\rho_{N_2}) + \rho_{N_2} + \Delta\rho_{N_2} \quad ;$$

$$\rho_s' - \rho_s = (M_f/M_h)(\Delta\rho_b - \Delta\rho_{N_2}) + \Delta\rho_{N_2} \quad . \tag{6}$$

For thorium-uranium or thorium-plutonium alloys, M_f/M_h may vary from 8 to 13, depending on composition. If $M_f/M_h = 13$, equation (6) gives

$$\Delta\rho_s = 13(0.000033 - 0.000041) + 0.000041$$

$$= 0.000031 \text{ g/cm}^3 \text{ max}$$

at 25°C. This is well below the experimental error and shows that the presence of bromobenzene vapor has a negligible effect on the measured densities.